As originally filed

## Cosurfactants based on aldehydes

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The present invention relates to condensation products of aldehydes with alcohols which have at least one other function from the group of hydroxyl, diol, amino and carboxyl functions.

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Surfactants are so-called amphiphilic molecules which have a hydrophobic moiety and a hydrophilic moiety in their molecular structure. As a result of this property, surfactants are able to form interfacial films and so-called micelles. These are aggregates of surfactants which form in aqueous solutions and can assume various forms (spheres, rods, disks). Micelles form above a certain concentration, the so-called critical micelle formation concentration (CMC). In addition, amphiphilic molecules have the property of forming interfacial films between hydrophobic and hydrophilic phases and thus, for example, having an emulsifying or foaming action.

Cosurfactants likewise have amphiphilic properties, although these are insufficient for being able to form micelles and interfacial films on their own. However, they are intercalated between the surfactants and bring about an increase in the packing density of the amphiphiles (surfactants and cosurfactants) in the structures formed thereby, such as micelles or interfaces. As a result, not only are the critical micelle formation concentration and the surface tension reduced, but also the interfacial tension between the aqueous surfactant solution and nonpolar substances such as, for example, oils, meaning that the absorption capacity of the surfactant system for these substances increases to the point of the formation of microemulsions. This results in a high solubilizing and emulsifying power, a higher cleaning capacity, and an increased stability of the emulsions and foams. If cosurfactants are used, micelles can be formed at a significantly lower surfactant concentration.

Further effects which are brought about as a result of the use of the cosurfactants and the resulting enhanced aggregation tendency of the amphiphiles are known. This is, firstly, the aggregation transformation of spherical to anisometric micellar associates. This structural

change in the micelles has effects on the rheology of the solutions containing the micelles, in particular in dilute solutions. At the same time, in the phase diagram, there is a shift of liquid crystalline structures present to lower concentrations, as a result of which a preferred formation of gel phases with higher packing density is observed. Consequently, even at concentrations of significantly < 10% by weight, lamellar micelle structures arise which are otherwise observed only at significantly higher concentrations. A further interesting phenomenon is the formation, in addition to the known liquid crystalline gel phases, of novel superstructures which have interesting application properties. Of particular interest here are vesicular phases and also so-called L<sub>3</sub> phases which have a sponge-like construction and have microemulsion-like properties. They can be used in dilute concentration ranges to adjust the viscosity.

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The prior art describes a number of compounds or classes of compounds which are suitable as cosurfactants.

C<sub>5</sub>-C<sub>10</sub>-alcohols exhibit advantageous properties, but are often not used due to their characteristic odor.

Alcohols with low degrees of ethoxylation, such as, for example, lauryl alcohol ethoxylates with low degrees of ethoxylation, diethylene glycol monohexyl ether or propylene glycol butyl ether, can lead to improved emulsifying power or foam stability in some surfactant systems, but have too low a polarity of the head group for surfactant formulations with a high anionic surfactant content.

25 Fatty acid ethanolamines are used, for example, for adjusting the viscosity in shampoos. However, they are suspected of forming nitrosamines.

G. J. Smith describes in Seifen, Ölen, Fette, Wachse, 105 (1979, pages 319 ff and 345 ff) the use of alkylamine oxides as cosurfactant in various applications. These too are suspected of containing nitrosamines. Through a lengthy, complex preparation technology, that can be largely avoided.

Analogously to the amine oxides, other zwitterionic surfactants, such as, for example, sulfobetaines or carboxylammoniobetaines, can also be used as cosurfactant. With these products, the formation of gel phases has proven to be very poor. Instead, however, they have the application advantage that the skin irritancy of corresponding surfactant mixtures is reduced.

WO 98/00418 discloses alkylene carbonates and their use as cosurfactants.

In the applications known to date, the ratio of cosurfactants to surfactants used varies, depending on the application, from about 1:20 to 1:2. In some cases, such as, for example, alkylamine oxides, the cosurfactant may also be used in higher concentrations.

It is an object of the present invention to provide compounds suitable as cosurfactants which do not have said disadvantages, in particular exhibit better cost efficiency, and are environmentally compatible and free from risks for humans.

We have found that this object is achieved by cyclic aldehyde derivatives of the formulae

in which the symbols X, Y, Z and R<sup>1</sup> to R<sup>13</sup> have the following meanings:

 $R^1$  is hydrogen or a linear or branched, substituted or unsubstituted  $C_3$ - $C_{29}$ -alkyl group or a linear or branched, substituted or unsubstituted  $C_3$ - $C_{29}$ -alkenyl group, where one or more carbon atoms in the alkyl or alkenyl chain may be replaced by -O-, -NR<sup>14</sup>, -C(O)NR<sup>15</sup>- or -S- and -O-O- and -S-S- are excluded;

R<sup>2</sup> is hydrogen or -CH<sub>3</sub>;

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 $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are, independently of one another, chosen from the group of substituents consisting of: H; -CN; -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents;

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0 = 0

and  $C_1$ - $C_5$ -alkyl groups which, at any desired point in the chain, may have 1 to 4 substituents from the group -OH; -SH; -CN;  $NR^{16}R^{17}$ ; -OR<sup>22</sup>; or 1 to 2 substituents from

the group consisting of -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; -OSO<sub>3</sub><sup>-</sup>; -SO<sub>3</sub><sup>-</sup>; -OPO<sub>3</sub><sup>2</sup>-; OPO(OR<sup>21</sup>)<sub>2</sub>; C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

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or

one of the substituent pairs  $R^3$ ,  $R^4$  and  $R^5$ ,  $R^6$  is =0;

 $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  are, independently of one another, chosen from the group of substituents consisting of: H; -CN; -NR<sup>16</sup>R<sup>17</sup>; -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; -OSO<sub>3</sub><sup>2</sup>; -OPO<sub>3</sub><sup>2</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>; C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents;

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and  $C_1$ - $C_5$ -alkyl groups which, at any desired point on the chain, may have 1 to 4 substituents from the group -OH; -SH; -CN;  $NR^{16}R^{17}$ ; -OR<sup>22</sup>; or 1 to 2 substituents from the group consisting of -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; -OSO<sub>3</sub><sup>-</sup>; -SO<sub>3</sub><sup>-</sup>; -OPO<sub>3</sub><sup>2-</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>;  $C_6H_5$ , in which one or more hydrogens may be replaced by substituents; and

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R<sup>11</sup> has, independently, the same meaning as R<sup>1</sup>;

 $R^{12}$  has, independently, the same meaning as  $R^2$ ;

 $R^{13}$  has, independently, the same meaning as  $R^3$ ,  $R^4$ ,  $R^5$  or  $R^6$ ;

R<sup>14</sup> is a linear or branched C<sub>1</sub>-C<sub>4</sub>-alkyl group;

20 R<sup>15</sup> is hydrogen or a linear or branched C<sub>1</sub>-C<sub>4</sub>-alkyl group;

 $R^{16}$ ,  $R^{17}$  are, independently of one another, hydrogen or a linear or branched  $C_1$ - $C_4$ -alkyl group;

 $R^{18}$  is chosen from the group consisting of  $C_1$ - $C_6$ -alkyl groups and ethyleneoxy groups -( $CH_2$ - $CH_2$ O-)<sub>p</sub>;

25  $R^{19}$ ,  $R^{20}$  have, independently, the same meaning as  $R^{16}$ ,  $R^{17}$ ;

R<sup>21</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group or -C<sub>6</sub>H<sub>5</sub>;

 $R^{22}$  is chosen from the group consisting of  $C_1$ - $C_{10}$ -alkyl groups, acyl groups - $C(O)R^{23}$  and the group consisting of ethyleneoxy groups - $(CH_2$ - $CH_2$ O- $)_q$ , propyleneoxy groups - $(CH(CH_3)$ - $CH_2$ O- $)_r$ , butyleneoxy groups - $(C_4H_9$ O- $)_s$ , and alkyleneoxy groups containing at least two of the abovementioned groups in the form of block or random copolymers and containing a total of at most 15 alkyleneoxy units;

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R<sup>23</sup> is a C<sub>1</sub>-C<sub>18</sub>-alkyl group;
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X and Y in formula I and II are, independently of one another, O, S, or NR<sup>24</sup>, Z in formula II is N;

R<sup>24</sup> is hydrogen or a C<sub>1</sub>-C<sub>4</sub>-alkyl group;

5 l, m and n are, independently of one another, 0 or 1;

p is an integer from 1 to 15;

q is an integer from 1 to 15;

r is an integer from 1 to 15;

s is an integer from 1 to 15;

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and where the aliphatic moiety of the compounds of the formula I or II which does not originate from the feed aldehyde, in cases where X, Y are =O and R<sup>3</sup>, R<sup>4</sup> or R<sup>5</sup>, R<sup>6</sup> are =O, must have at least 2 carbon atoms, and in all other cases must have at least 3 carbon atoms.

The compounds of the formulae I and II are highly suitable for use as cosurfactants in the customary washing and cleaning formulations known to the person skilled in the art.

The compounds according to the formulae I and II are prepared by condensation of aldehydes with polyfunctional compounds whose functional groups are chosen from the group of hydroxyl, thiol, carboxyl and primary and secondary amino functions. There must be at least two functional groups, which may be identical or different, present in the polyfunctional compound.

The aldehydes to be used are linear or branched aliphatic  $C_4$ - $C_{30}$ -aldehydes, preferably  $C_6$ - $C_{18}$ -aldehydes. These aldehydes have an average degree of branching of from 0 to 2.5, preferably 0.2 to 1.6. The degree of branching here is defined as (number of methyl groups per molecule) -1. Since the aliphatic chain radical of the aldehyde joined to the carbonyl function corresponds to the radical  $R^1$  in the formulae I and II, this last-named radical also has a corresponding degree of branching. The alkyl chain can have further substituents which increase the suitability of the molecule as a cosurfactant, or at least do not adversely affect it. Such substituents are known to the person skilled in the art. Preferably, no further substituents are present on the alkyl chain. Examples of aldehydes which can be used include butanal, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, dodecanal, tridecanal, tetradecanal and hexadecanal. For all of the abovementioned aldehydes, it is possible to use either the unbranched n-form or branched isomers. In general, use is made of isomer mixtures of the aldehydes used which have the desired average degree of branching.

It is also possible to use mixtures of aldehydes of varying carbon number and to use the resulting product mixtures as cosurfactants. This embodiment is preferred in accordance with the invention. Particular preference is given here to the use of a mixture of  $C_{12}$ -/ $C_{14}$ -aldehydes.

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Also preferred in accordance with the invention is the use of the so-called Guerbet aldehydes and their unsaturated analogs. These are aldehydes with branching in the 2 position. Examples include 2-ethylhexanal, 2-ethylhex-2-enal, 2-propylhexanal, 2-propylheptanal, 2-propylhept-2-enal, 2-butyloctanal, 2-butyloct-2-enal, 2-pentylnonanal and 2-pentylnon-2-enal. Saturated aldehydes are preferred.

The polyfunctional starting materials to be reacted with the aldehyde are the substances listed below.

#### 15 Polyols:

Suitable polyols are linear and branched aliphatic  $C_3$ - $C_6$ -polyols with at least two hydroxyl functions, preferably 2 to 5 hydroxyl functions, in particular 2 to 4 hydroxyl functions. As well as the hydroxyl functions, further functional groups may be present which are chosen from the group -SH; -CN;  $NR^{16}R^{17}$ ; -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; -OSO<sub>3</sub><sup>-</sup>; -SO<sub>3</sub><sup>-</sup>; -OPO<sub>3</sub><sup>2-</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>; -OR<sup>22</sup>;  $C_6H_5$ , in which one or more hydrogens may be replaced by substituents; and

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Examples of suitable polyols include glycerol, tartaric acid, diethyl tartrate, trimethylolpropane, fructose, cyclohexanediol, sucrose, tetrahydroxybutane.

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#### Alkanolamines:

Suitable alkanolamines are linear and branched aliphatic  $C_3$ - $C_6$ -alkanolamines with at least one primary or secondary amino function and one hydroxyl function. A maximum of 4 further hydroxyl or amino functions may be present, preferably the alkanolamine has exactly one amino function. Further substituents may be present from the group: -SH; -CN; -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; -OSO<sub>3</sub><sup>-</sup>; -SO<sub>3</sub><sup>-</sup>; -OPO<sub>3</sub><sup>2-</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>; -OR<sup>22</sup>; -C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

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Examples of suitable alkanolamines include trimethylolmethylamine, diethanolamine, propanolamine, dipropanolamine, amino sugars, amino acids, such as, for example, sarcosine, serine and threonine.

#### 5 Thiols:

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Suitable thiols are linear and branched aliphatic  $C_3$ - $C_6$ -thiols with one thiol function and one hydroxyl function. Four further hydroxyl or thiol functions may be present. Preferably, the thiol has exactly one SH function. Further substituents may be present from the group: -OH; -SH; -CN;  $NR^{16}R^{17}$ ; -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>  $R^{20}$ ; -OSO<sub>3</sub><sup>-</sup>; -SO<sub>3</sub><sup>-</sup>; -OPO<sub>3</sub><sup>2-</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>; -OR<sup>22</sup>; -C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

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Examples of suitable thiols are mercaptoethanol, mercaptolactic acid, mercaptoglycolic acid, thiosalicylic acid, mercaptosuccinic acid, 3-mercapto-1,2-propanediol, cysteine, N-acetylcysteine, 3-mercaptopropionic acid, penicillamine, dithiothreitol.

### Hydroxycarboxylic acids:

Suitable hydroxycarboxylic acids are linear and branched aliphatic  $C_3$ - $C_6$ -hydroxycarboxylic acids with one hydroxyl function and one carboxyl function. Four further hydroxyl or carboxyl functions may be present. Preferably, the molecule has exactly one carboxyl function. Further substituents may be present from the group: -SH; -CN;  $NR^{16}R^{17}$ ; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; -OSO<sub>3</sub>; -SO<sub>3</sub>; -OPO<sub>3</sub><sup>2-</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>; -OR<sup>22</sup>; -C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

Examples of suitable hydroxycarboxylic acids include lactic acid, citric acid, glycolic acid, tartaric acid, glyceric acid, malic acid and salicylic acid.

#### Diamines:

It is possible to use linear and branched aliphatic C<sub>3</sub>-C<sub>6</sub>-diamines having 2 to 6 primary or secondary amino functions. Preferably, the diamines have 2 to 4 primary or secondary

amino functions. Further substituents may be present from the group: -OH; -SH; -CN; -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; -OSO<sub>3</sub>; -SO<sub>3</sub>; -OPO<sub>3</sub><sup>2-</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>; -OR<sup>22</sup>; -C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

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Examples of suitable diamines include propylenediamine, triethylenetriamine, triethylenetetramine, N-aminopropylethylenediamine (N<sub>3</sub>-amine) and N,N'-bis(aminopropyl)ethylenediamine (N<sub>4</sub> amine), hydroxyethylethylenediamine.

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### **Aminothiols:**

Suitable aminothiols are linear and branched aliphatic C<sub>3</sub>-C<sub>6</sub>-aminothiols with at least one primary or secondary amino function and one thiol function. Preferably, the amino thiol used has exactly one primary or secondary amino function and exactly one thiol function. Further substituents may be present from the group: -OH; -CN; -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>; -OSO<sub>3</sub><sup>-</sup>; -SO<sub>3</sub><sup>-</sup>; -OPO<sub>3</sub><sup>2</sup><sup>-</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>; -OR<sup>22</sup>; -C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

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Examples include cysteine and tyrosine and mercaptopropylamine.

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#### Amino acids:

Suitable amino acids are linear and branched aliphatic C<sub>3</sub>-C<sub>6</sub>-amino acids with at least one primary or secondary amino function and one carboxyl function. Preferably, the amino acids used according to the invention contain one primary or secondary amino function. Examples include iminodiacetic acid HN(CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub> and ethylenediamine triacetic acid, and the amino acids alanine, arginine, asparagine, aspartic acid, cysteine, glutamine, glutaminic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine, valine and N-phosphonomethylglycine.

## 30 <u>Dithiols:</u>

Suitable dithiols are linear and branched aliphatic  $C_3$ - $C_6$ -dithiols with at least two thiol functions. Preferably, the dithiol has exactly two thiol functions. Further substituents may be present from the group: -OH; -CN;  $NR^{16}R^{17}$ ; -C(O)OH; -C(O)OR<sup>18</sup>; -C(O)NR<sup>19</sup>R<sup>20</sup>;

-OSO<sub>3</sub><sup>-</sup>; -SO<sub>3</sub><sup>-</sup>; -OPO<sub>3</sub><sup>2-</sup>; OPO(OR<sup>21</sup>)<sub>2</sub>; -OR<sup>22</sup>; -C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

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0 = 0

The alkyleneoxy substituents which may be present in the cosurfactants of the formulae I and II used according to the invention (see, for example, definition of R<sup>22</sup>) may be pure ethyleneoxy, propyleneoxy or butyleneoxy substituents. Butyleneoxy substituents may be those derived from 1-butene, 2-butene or isobutene. Within the group of butyleneoxy substituents, preference is given to the group -(CH<sub>2</sub>CH(C<sub>2</sub>H<sub>5</sub>)-O) derived from 1-butene.

These substituents can, however, also consist of mixtures of ethyleneoxy, propyleneoxy or butyleneoxy units, for example as a random oligo/polymer or as a block copolymer. Preferably, said alkyleneoxy substituents are pure ethyleneoxy groups or terminally capped ethyleneoxy groups.

If an individual compound is present which contains alkyleneoxy substituents, then this contains a whole-number amount of alkyleneoxy units in the amounts given in the description. If mixtures of different compounds with alkyleneoxy substituents are present, these are often mixtures in which the amount of alkyleneoxy substituents is, on average, no longer a whole number.

-C<sub>6</sub>H<sub>5</sub> designates a phenyl group.

Preferred molecules of the formulae I and II are those in which one or more of the symbols X, Y and Z, one or more of the substituents  $R^1$  to  $R^{13}$ , and one or more of the symbols I, m and n have the following meanings:

 $R^1$  is a linear or branched  $C_5$ - $C_{17}$ -alkyl group or a linear or branched  $C_3$ - $C_{17}$ -alkenyl group, where one or more carbon atoms in the alkyl chain may be replaced by O or  $NR^{14}$  and -O-O- is excluded;

 $R^2$  is -H;

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R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are, independently of one another, chosen from the group consisting of: -H; -C(O)OH; -C(O)OR<sup>18</sup>;

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and  $C_1$ - $C_5$ -alkyl groups which, at any desired position on the chain, may have 1 or 2 substituents from the group -OH; -CN;  $NR^{16}R^{17}$ ; -OR<sup>22</sup>; or 1 substituent from the group consisting of -C(O)OH; -C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

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or

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one of the substituent pairs  $R^3$ ,  $R^4$  and  $R^5$ ,  $R^6$  is =0;

R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> are, independently of one another, chosen from the group consisting of: -H; -NR<sup>16</sup>R<sup>17</sup>; -C(O)OH; -C(O)OR<sup>18</sup>;

$$\bigcup_{0} = 0$$

and  $C_1$ - $C_5$ -alkyl groups which, at any desired position on the chain, may have 1 or 2 substituents from the group -OH; -CN;  $NR^{16}R^{17}$ ; -OR<sup>22</sup>; or 1 substituent from the group consisting of -C(O)OH; -C<sub>6</sub>H<sub>5</sub>, in which one or more hydrogens may be replaced by substituents; and

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0 = 0

- R<sup>11</sup> has, independently, the same meaning as R<sup>1</sup>;

 $R^{12}$  has, independently, the same meaning as  $R^2$ ;

R<sup>13</sup> has, independently, the same meaning as R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> or R<sup>6</sup>;

R<sup>14</sup> is a linear or branched C<sub>1</sub>-C<sub>4</sub>-alkyl group;

 $R^{16}$ ,  $R^{17}$  are, independently of one another, hydrogen or a linear or branched  $C_1$ - $C_4$ -alkyl group;

R<sup>18</sup> is chosen from the group consisting of  $C_1$ - $C_6$ -alkyl groups and ethyleneoxy groups -( $CH_2$ - $CH_2$ O-)<sub>p</sub>;

 $R^{22}$  is chosen from the group consisting of  $C_1$ - $C_4$ -alkyl groups, acyl groups - $C(O)R^{23}$  and the group consisting of ethyleneoxy groups - $(CH_2-CH_2O_1)_q$ , propyleneoxy groups - $(CH(CH_3)-CH_2O_1)_r$  and butyleneoxy groups - $(C_4H_9O_1)_s$ , and mixed alkyleneoxy groups;

30  $R^{23}$  is a  $C_1$ - $C_{18}$ -alkyl group;

X and Y in the formula I and II are, independently of one another, O or NR<sup>24</sup>, Z in formula II is N;

R<sup>24</sup> is hydrogen or a C<sub>1</sub>-C<sub>4</sub>-alkyl group;

1, m and n are, independently of one another, 0 or 1;

p is an integer from 1 to 15;

q is an integer from 1 to 10;

r is an integer from 1 to 10;

s is an integer from 1 to 10;

and where the aliphatic moiety of the compounds of the formula I or II which does not originate from the feed aldehyde, in cases where X, Y are =0 and R<sup>3</sup>, R<sup>4</sup> or R<sup>5</sup>, R<sup>6</sup> are =0, must have at least 2 carbon atoms, and in all other cases must have at least 3 carbon atoms.

In this connection, it is preferred if all of the substituents  $R^1$  to  $R^{13}$  and symbols X, Y and Z and l, m, and n have the meanings given above.

More preferred are also the compounds of the formulae I and II, in which one or more of the symbols X, Y, Z and l, m, and n and also one or more of the substituents  $R^1$  to  $R^{13}$  have the following meanings:

R<sup>1</sup> is a linear or branched  $C_5$ - $C_{17}$ -alkyl group or a linear or branched  $C_5$ - $C_{17}$ -alkenyl group;  $R^2$  is -H;

 $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are, independently of one another, chosen from the group consisting of: -H; -C(O)OH; and C<sub>1</sub>-C<sub>3</sub>-alkyl groups which can have, at any desired point on the chain, 1 or 2 substituents from the group -OH; -NR<sup>16</sup>R<sup>17</sup>; -OR<sup>22</sup>; or 1 substituent from the group consisting of -C(O)OH; and

$$\bigcup_{0} = 0$$

or

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one of the substituent pairs R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>, R<sup>6</sup> is =O;

R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> are, independently of one another, chosen from the group consisting of:
-H; -NR<sup>16</sup>R<sup>17</sup>; -C(O)OH; and C<sub>1</sub>-C<sub>3</sub>-alkyl groups which, at any desired point on the chain, can have 1 or 2 substituents from the group -OH; NR<sup>16</sup>R<sup>17</sup>; or 1 substituent from the group consisting of -C(O)OH; and

$$\bigcirc 0 = 0$$

R<sup>11</sup> has, independently, the same meaning as R<sup>1</sup>;

R<sup>12</sup> has, independently, the same meaning as R<sup>2</sup>;

R<sup>13</sup> has, independently, the same meaning as R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> or R<sup>6</sup>;

 $R^{16}$ ,  $R^{17}$  are, independently of one another, hydrogen or a linear or branched  $C_1$ - $C_4$ -alkyl group;

 $R^{22}$  is chosen from the group consisting of  $C_1$ - $C_4$ -alkyl groups, acyl groups - $C(O)R^{23}$  and the group consisting of ethyleneoxy groups - $(CH_2-CH_2O_1)_q$ , propyleneoxy groups - $(CH(CH_3)-CH_2O_1)_r$  and butyleneoxy groups - $(CH_2-CH_2O_1)_r$  and butyleneoxy groups - $(CH_2-CH_2O_1)_r$  and mixed alkyleneoxy

10 groups;

R<sup>23</sup> is a C<sub>1</sub>-C<sub>18</sub>-alkyl group;

X and Y in formula I and II are, independently of one another, O or NR<sup>24</sup>, Z in formula II is N;

 $R^{24}$  is hydrogen or a  $C_1$ - $C_4$ -alkyl group;

15 l, m and n are, independently of one another, 0 or 1;

q is an integer from 1 to 10;

r is an integer from 1 to 10;

s is an integer from 1 to 10;

and where the aliphatic moiety of the compounds of the formula I or II which does not originate from the feed aldehyde in cases where X, Y are =0 and R<sup>3</sup>, R<sup>4</sup> or R<sup>5</sup>, R<sup>6</sup> are =0 must have at least 2 carbon atoms, and in all other cases must have at least 3 carbon atoms.

In this connection, it is preferred if all of the substituents  $R^1$  to  $R^{13}$  and the symbols X, Y and Z and I, m, and n have the meanings given above.

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Even more preferred are also the compounds of the formulae I and II in which one or more of the symbols X, Y, Z and l, m, and n and also one or more of the substituents  $R^1$  to  $R^{13}$  have the following meanings:

 $R^1$  is a linear or branched  $C_3$ - $C_{21}$ -alkyl group or a linear or branched  $C_3$ - $C_{21}$ -alkenyl group;  $R^2$  is -H;

 $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are, independently of one another, chosen from the group consisting of: -H; -C(O)OH; and C<sub>1</sub>-C<sub>3</sub>-alkyl groups which may have, at any desired point on the chain, 1 or 2 substituents from the group -OH; -NR<sup>16</sup>R<sup>17</sup>; -OR<sup>22</sup>; or 1 substituent of the type -C(O)OH; or

one of the substituent pairs  $R^3$ ,  $R^4$  and  $R^5$ ,  $R^6$  is =0;

 $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  are, independently of one another, chosen from the group consisting of: -H; -NR<sup>16</sup>R<sup>17</sup>; -C(O)OH; and C<sub>1</sub>-C<sub>3</sub>-alkyl groups which may have, at any desired point on the chain, 1 or 2 substituents from the group -OH; NR<sup>16</sup>R<sup>17</sup>; or 1 substituent of the type -C(O)OH;

 $R^{11}$  has, independently, the same meaning as  $R^{1}$ ;

 $R^{12}$  has, independently, the same meaning as  $R^2$ ;

R<sup>13</sup> has, independently, the same meaning as R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> or R<sup>6</sup>;

 $R^{16}$ ,  $R^{17}$  are, independently of one another, hydrogen or a linear or branched  $C_1$ - $C_4$ -alkyl group;

10  $R^{22}$  is chosen from the group consisting of  $C_1$ - $C_4$ -alkyl groups and ethyleneoxy groups - $(CH_2$ - $CH_2$ O- $)_q$ ;

X and Y in formula I and II are, independently of one another, O, S, or NR<sup>24</sup>, Z in formula II is N;

R<sup>24</sup> is hydrogen or a C<sub>1</sub>-C<sub>4</sub>-alkyl group;

15 l, m and n are, independently of one another, 0 or 1;

q is an integer from 3 to 8;

and where the aliphatic moiety of the compounds of the formula I or II which does not originate from the feed aldehyde in cases where X, Y are =0 and  $R^3$ ,  $R^4$  or  $R^5$ ,  $R^6$  are =0 must have at least 2 carbon atoms, and in all other cases must have at least 3 carbon atoms.

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In this connection, it is preferred if all of the substituents  $R^1$  to  $R^{13}$  and the symbols X, Y and Z and I, m, and n have the meanings given above.

Particular preference is given to the following compounds:

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2-(1-ethylpentyl)-[1,3]dioxolan-4-one

3,5-bis-(1-ethylpentyl)-7a-hydroxymethyldihydrooxazolo[3,4-c] oxazole

(2)

7a-hydroxymethyl-3,5-dinonyldihydrooxazolo[3,4-c]oxazole

$$HO \longrightarrow O \longrightarrow H$$

(4)

2-(1-ethylpentyl)-4,4-di(hydroxymethyl)oxazolidine

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4,4-di(hydroxymethyl)-2-nonyloxazolidine and

2-(1-propylhexyl)4,4-di(hydroxymethyl)oxazolidine (6);

5 7a-hydroxymethyl-3,5-di(dodecyl)dihydrooxazolo[3,4-c]oxazole (7);

7a-hydroxymethyl-3,5-di(tetradecyl)dihydrooxazolo[3,4-c]oxazole (8);

7a-hydroxymethyl-3,5-di(undecyl)dihydrooxazolo[3,4-c]oxazole (9);

7a-hydroxymethyl-3,5-di(tridecyl)dihydrooxazolo[3,4-c]oxazole (10);

4,4-di(hydroxymethyl)-2-dodecyloxazolidine (11);

4,4-di(hydroxymethyl)-2-tetradecyloxazolidine (12);

4,4-di(hydroxymethyl)-2-undecyloxazolidine (13);

4,4-di(hydroxymethyl)-2-tridecyloxazolidine (14);

2-(1-propylhexyl)-[1,3]-dioxolan-4-one (15)

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2-(1-propylhexenyl)-[1,3]dioxolan-4-one

(16)

7 a-hydroxymethyl-3, 5-di(1-propylhexenyl) dihydrooxazolo [3,4-c] oxazole

(17)

4, 4- di (hydroxymethyl) - 2- (1-propylhexenyl) oxazolidine

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(18)

Mixtures of (9) and (10), mixtures of (13) and (14), mixtures of (7) and (8) and mixtures of (11) and (12) are likewise the subject-matter of the most preferred embodiment of the present invention.

A subject-matter of the most preferred embodiment of the present invention are likewise the adducts of the compounds (1) to (18) having 3 to 10 ethylene oxide units and mixtures thereof. In connection with the present invention, the term "mixtures" is understood as meaning both mixtures of adducts of a compound (1) to (18) with varying amounts of added ethylene oxide units, and also mixtures of ethylene oxide adducts of various compounds (1) to (18).

The invention further provides for the use of the compounds of the formulae I and II and the preferred compounds derived therefrom as specified above as cosurfactant.

The compounds of the formulae I and II used according to the invention as cosurfactants are prepared by customary condensation reactions known to the person skilled in the art. The aldehyde and the substance or the substance mixture to be reacted therewith, which is chosen from the abovementioned group of substances, are, optionally in the presence of a suitable acid, reacted together in a suitable solvent, such as, for example, toluene, chloroform or methylene chloride. Suitable acids are the customary Lewis and Brönsted acids known to the person skilled in the art which can be used in gaseous, liquid or solid form. Examples include HCl, sulfuric acid, p-toluenesulfonic acid, p-toluenesulfonic acid pyridinium salt and acidic ion exchangers, for example Amberlyst®15 and Serdolit Red. Alternatively, the starting material to be reacted with the aldehyde can be added to an initial charge of the aldehyde, which may be dissolved in a solvent. This is advantageous particularly in the case of hydroxycarboxylic acids, which can be added as aqueous solution to the reaction mixture. Preferably, the water which forms during the condensation is separated off by distillation. Preference is given to working without solvents. If a solvent is used, the water can be separated off by azeotropic distillation, for example using a water separator.

The substances of the formulae I and II according to the invention to be used as cosurfactants are suitable for use in industrial, institutional or domestic detergents and cleaners, and also in the so-called bodycare sector, namely body-cleansing and bodycare compositions.

## Further applications are:

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- humectants, in particular for the printing industry.
- cosmetic, pharmaceutical and crop protection formulations. Suitable crop protection formulations are described, for example in EP-A-0 050 228. Further ingredients customary for crop protection compositions may also be present.
  - paints, coating compositions, inks, pigment preparations and adhesives in the coating and polymer film industry.
- 30 leather fat-liquoring compositions.
  - formulations for the textile industry, such as leveling agents or formulations for yarn cleaning.
  - fiber processing and auxiliaries for the paper and pulp industry.
  - metal processing, such as metal refining and electroplating sector.
- 35 food industry.
  - water treatment and drinking water production.
  - fermentation.

- mineral processing and dust control.
- building auxiliaries.
- emulsion polymerization and preparation of dispersions.
- coolants and lubricants.

The determents a

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The detergents are in solid, liquid, gel or paste form. The materials in solid form include powders and compacts, for example granulates and shaped bodies such as tablets.

The detergents comprise 0.1 to 40% by weight, in particular 0.5 to 30% by weight, very particularly 1 to 20% by weight, based on the total amount of the formulation, of at least one substance of the formulae I and/or II. Further constituents are listed below.

Detergent formulations usually comprise ingredients such as surfactants, builders, fragrances and dyes, complexing agents, polymers and other ingredients. Typical formulations are described, for example, in WO 01/32820. Further ingredients suitable for various applications are described in EP-A-0 620 270, WO 95/27034, EP-A-0 681 865, EP-A-0 616 026, EP-A-0 616 028, DE-A-42 37 178 and US 5,340,495, for example.

For the purposes of this invention, detergents are generally used for the washing of materials of greater or lesser flexibility, preferably those which contain or consist of natural, synthetic or semisynthetic fiber materials and which consequently usually have at least partially a textile character. The materials which contain or consist of fibers can, in principle, be in any form which exists in use or for the preparation and processing. For example, fibers may be unarranged in the form of staple or aggregate, arranged in the form of threads, yarns, twines, or in the form of fabrics, such as nonwovens, loden materials or felt, wovens, knits in all conceivable types of weave.

These may be raw fibers or fibers in any stages of processing and may be natural protein or cellulose fibers, such as wool, silk, cotton, sisal, hemp, coconut fibers or synthetic fibers, such as, for example, polyester, polyamide or polyacrylonitrile fibers.

Detergents comprising cosurfactants according to the invention can also be used for cleaning fiber-containing materials, such as e.g. backed carpets with cut or uncut pile.

35 The compositions of the detergents are preferably adapted to the different purposes, as is familiar to the person skilled in the art from the prior art. For this purpose, all auxiliaries and

additives corresponding to the purpose and known from the prior art can be added to the detergents.

In addition to the cosurfactants according to the invention, the following may, for example, be present in detergents:

- builders and cobuilders, such as polyphosphates, zeolites, polycarboxylates, phosphonates or complexing agents
- ionic surfactants, such as alcohol sulfates/ether sulfates, alkylbenzenesulfonates, α-olefinsulfonates and other alcohol sulfates/ether sulfates
  - nonionic surfactants, alcohol alkoxyates such as alkylamine alkoxylates, alkyl polyglucosides
  - optical brighteners

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- color transfer inhibitors, such as polyvinylpyrrolidone of molar masses 8000 to 70 000,
   vinylimidazole/vinylpyrrolidone copolymers with a molar ratio of the monomers of from 1:10 to 2:1 and molar masses of from 8000 to 70 000, and poly-4-vinylpyridine N-oxides with molar masses of from 8000 to 70 000
  - extenders, such as sodium sulfate or magnesium sulfate
  - soil release agent
- 20 incrustation inhibitors
  - bleaching systems, comprising bleach, such as perborate, percarbonate and bleach activators, such as tetraacetylethylenediamine, and also bleach stabilizers
  - perfume (oils)
  - foam suppressors, such as silicone oils
- 25 enzymes, such as amylases, lipases, cellulases, proteases
  - alkali metal donors, such as soluble alkali metal silicates, e.g. pentasodium methasilicate, sodium carbonate.

Solvents, such as ethanol, isopropanol, 1,2-propylene glycol, butyl glycol etc., can, for example, additionally be used in liquid detergents.

In tablet detergents, it is additionally possible to use tableting auxiliaries, such as polyethylene glycols with molar masses of more than 1000 g/mol, polymer dispersions, and tablet disintegrants, such as cellulose derivatives, crosslinked polyvinylpyrrolidone, crosslinked polyacrylates or combinations of acids, such as citric acid and sodium bicarbonate. A detailed list of possible ingredients is given below.

In some cases, it may be expedient to combine the cosurfactants used according to the invention with other cosurfactants or with amphoteric surfactants, such as, for example, alkylamine oxides, or betaines.

Another class of nonionic surfactants are alkyl polyglucosides having 6 to 22, preferably 10 to 18, carbon atoms in the alkyl chain. These compounds generally contain 1 to 20, preferably 1.1 to 5, glucoside units.

Another class of nonionic surfactants are N-alkylglucamides of the structures

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where  $B^1$  is a  $C_{6^-}$  to  $C_{22^-}$ alkyl,  $B^2$  is hydrogen or  $C_{1^-}$  to  $C_4$ -alkyl and D is a polyhydroxyalkyl radical having 5 to 12 carbon atoms and at least 3 hydroxyl groups. Preferably,  $B^1$  is  $C_{10^-}$  to  $C_{18^-}$ alkyl,  $B^2$  is  $CH_3$  and D is a  $C_{5^-}$  or  $C_6$ -radical. For example, such compounds are obtained by the acylation of reductively aminated sugars with acid chlorides of  $C_{10^-}$  to  $C_{18^-}$ carboxylic acids.

Further suitable nonionic surfactants are the terminally capped fatty acid amide alkoxylates, known from WO-A 95/11225, of the formula

$$R^{1}$$
-CO-NH- (CH<sub>2</sub>)<sub>y</sub>-O- (A<sup>1</sup>O)<sub>x</sub>-R<sup>2</sup>

in which

25  $R^1$  is a  $C_5$ - to  $C_{21}$ -alkyl or alkenyl radical,

R<sup>2</sup> is a C<sub>l</sub>- to C<sub>4</sub>-alkyl group,

 $A^1$  is  $C_2$ - to  $C_4$ -alkylene,

y is the number 2 or 3 and

x has a value from 1 to 6.

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Examples of such compounds are the reaction products of n-butyltriglycolamine of the formula  $H_2N$ - $(CH_2$ - $CH_2$ - $O)_3$ - $C_4H_9$  with methyl dodecanoate or the reaction products of ethyltetraglycolamine of the formula  $H_2N$ - $(CH_2$ - $CH_2$ - $O)_4$ - $C_2H_5$  with a standard commercial mixture of saturated  $C_8$ - to  $C_{18}$ -fatty acid methyl esters.

Further suitable nonionic surfactants are also block copolymers of ethylene oxide, propylene oxide and/or butylene oxide (Pluronic® and Tetronic® brands from BASF), polyhydroxy or polyalkoxy fatty acid derivatives, such as polyhydroxy fatty acid amides, N-alkoxy- or N-aryloxypolyhydroxy fatty acid amides, fatty acid amide ethoxylates, in particular terminally capped ones, and fatty acid alkanolamide alkoxylates.

The additional nonionic surfactants are present in the detergents comprising the cosurfactants used in accordance with the invention preferably in an amount of from 0.01 to 30% by weight, in particular 0.1 to 25% by weight, especially 0.5 to 20% by weight.

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It is also possible to use individual nonionic surfactants or a combination of different nonionic surfactants. The nonionic surfactants used may come from only one class, in particular only alkoxylated  $C_{8}$ - to  $C_{22}$ -alcohols, or surfactant mixtures from different classes can be used.

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Suitable anionic surfactants are, for example, fatty alcohol sulfates of fatty alcohols having 8 to 22, preferably 10 to 18, carbon atoms, C<sub>12</sub>-C<sub>18</sub>-alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate.

Further suitable anionic surfactants are sulfated ethoxylated C<sub>8</sub>- to C<sub>22</sub>-alcohols (alkyl ether 20 sulfates) or soluble salts thereof. Compounds of this type are prepared, for example, by firstly alkoxylating a C<sub>8</sub>- to C<sub>22</sub>-, preferably a C<sub>10</sub>- to C<sub>18</sub>-alcohol, e.g. a fatty alcohol, and then sulfating the alkoxylation product. For the alkoxylation, preference is given to using ethylene oxide, 1 to 50 mol, preferably 1 to 20 mol, of ethylene oxide being used per mole 25 of alcohol. The alkoxylation of the alcohols can, however, also be carried out with propylene oxide on its own and optionally butylene oxide. Furthermore, also suitable are those alkylated C<sub>8</sub>- to C<sub>22</sub>-alcohols which contain ethylene oxide and propylene oxide or ethylene oxide and butylene oxide or ethylene oxide and propylene oxide and butylene oxide. The alkoxylated C<sub>8</sub>- to C<sub>22</sub>-alcohols can contain the ethylene oxide, propylene oxide and butylene oxide units in the form of blocks or in random distribution. Depending on the 30 nature of the alkoxylation catalyst, alkyl ether sulfates can be obtained with a broad or narrow alkylene oxide homolog distribution.

Further suitable anionic surfactants are alkanesulfonates, such as  $C_{8}$ - to  $C_{24}$ -, preferably  $C_{10}$ - to  $C_{18}$ -alkanesulfonates, and soaps, such as, for example, the Na and K salts of saturated and/or unsaturated  $C_{8}$ - to  $C_{24}$ -carboxylic acids.

Further suitable anionic surfactants are linear  $C_8$ - to  $C_{20}$ -alkylbenzenesulfonates ("LAS"), preferably linear  $C_9$ - to  $C_{13}$ -alkylbenzenesulfonates and -alkyltoluenesulfonates.

Further suitable anionic surfactants are also C<sub>8</sub>- to C<sub>24</sub>-olefinsulfonates and -disulfonates, which may also represent mixtures of alklene- and hydroxyalkanesulfonates or -disulfonates, alkyl ester sulfonates, sulfonated polycarboxylic acids, alkylglycerol sulfonates, fatty acid glycerol ester sulfonates, alkylphenol polyglycol ether sulfates, paraffinsulfonates having about 20 to about 50 carbon atoms (based on paraffin or paraffin mixtures obtained from natural sources), alkyl phosphates, acyl isethionates, acyl taurates, acyl methyltaurates, alkylsuccinic acids, alkenylsuccinic acids or half-esters or half-amides thereof, alkylsulfosuccinic acids or amides thereof, mono- and diesters of sulfosuccinic acids, acyl sarcosinates, sulfated alkyl polyglucosides, alkyl polyglycol carboxylates and hydroxyalkyl sarcosinates.

The anionic surfactants are preferably added to the detergent in the form of salts. Suitable cations in these salts are alkali metal ions, such as sodium, potassium and lithium and ammonium salts, such as, e.g. hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium salts.

The anionic surfactants are present in the detergents comprising the cosurfactants according to the invention preferably in an amount of up to 30% by weight, for example from 0.1 to 30% by weight, especially 1 to 25% by weight, in particular 3 to 10% by weight. If C<sub>9</sub>- to C<sub>20</sub> linear alkyl-benzenesulfonates (LAS) are co-used, these are usually employed in an amount up to 15% by weight, in particular up to 10% by weight.

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It is possible to use individual anionic surfactants or a combination of different anionic surfactants. The anionic surfactants used may be from only one class, for example only fatty alcohol sulfates or only alkylbenzenesulfonates, although it is also possible to use surfactant mixtures from different classes, e.g. a mixture of fatty alcohol sulfates and alkylbenzenesulfonates.

In addition, the surfactant mixtures comprising the cosurfactants to be used according to the invention can be combined with cationic surfactants, customarily in an amount up to 25% by weight, preferably 1 to 15% by weight, for example  $C_8$ - to  $C_{16}$ -dialkyldimethylammonium salts, dialkoxydimethylammonium salts or imidazolinium salts with a long-chain alkyl radical; and/or with amphoteric surfactants, customarily in an amount up to 15% by weight, preferably 1 to 10% by weight, for example derivatives of

secondary or tertiary amines, such as, e.g. C<sub>6</sub>-C<sub>18</sub>-alkylbetaines or C<sub>6</sub>-C<sub>15</sub>-alkylsulfobetaines or alkylamidobetaines or amine oxides, such as alkyldimethylamine oxides.

5 It is also possible to use cationic surfactants as are described in WO 99/19435.

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The mixtures comprising the cosurfactants to be used in accordance with the invention are usually combined with builders (sequestering agents), such as, for example, polyphosphates, polycarboxylates, phosphonates, complexing agents, e.g. methylglycinediacetic acid and salts thereof, nitrilotriacetic acid and salts thereof, ethylenediaminetetraacetic acid and salts thereof, and optionally with cobuilders.

Individual builder substances which are highly suitable for the combination with mixtures comprising the cosurfactants to be used in accordance with the invention may be listed below:

Suitable inorganic builders are primarily crystalline or amorphous alumosilicates having ion-exchanging properties, such as, in particular, zeolites. Various types of zeolites are suitable, in particular zeolites A, X, B, P, MAP and HS in their Na form or in forms in which Na is partially replaced by other cations, such as Li, K, Ca, Mg or ammonium. Suitable zeolites are described, for example, in US-A-4604224.

Examples of crystalline silicates which are suitable as builders are disilicates or phyllosilicates, e.g. δ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> or β-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>. The silicates can be used in the form of their alkali metal, alkaline earth metal or ammonium salts, preferably as Na, Li and Mg silicates. Amorphous silicates, such as, for example, sodium metasilicate, which has a polymeric structure, or amorphous disilicate can likewise be used.

Suitable carbonate-based inorganic builder substances are carbonates and hydrogencarbonates. These can be used in the form of their alkali metal, alkaline earth metal or ammonium salts. Preference is given to using Na, Li and Mg carbonates or hydrogencarbonates, in particular sodium carbonate and/or sodium hydrogencarbonate.

Customary phosphates used as inorganic builders are alkali metal orthophosphates and/or polyphosphates, such as, for example, pentasodium triphosphate.

35 Said builder components can be used individually or in mixtures with one another.

In addition, in many cases, it is expedient to add cobuilders to the detergents comprising the cosurfactants to be used in accordance with the invention. Examples of suitable substances are listed below:

In a preferred embodiment, the detergents comprising the cosurfactants to be used in accordance with the invention comprise, in addition to the inorganic builders, 0.05 to 20% by weight, in particular 1 to 10% by weight, of organic cobuilders in the form of low molecular weight, oligomeric or polymeric carboxylic acids, in particular polycarboxylic acids, or phosphonic acids or salts thereof, in particular Na or K salts.

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Low molecular weight carboxylic acids or phosphonic acids suitable as organic cobuilders are, for example, phosphonic acids, such as, for example, 1-hydroxyethane-1,1-diphosphonic acid, amino-tris(methylenephosphonic acid), ethylenediaminetetra-(methylenephosphonic acid) and diethylenetriaminepenta(methylenephosphonic acid);

 $C_4$ - to  $C_{20}$ -di-, -tri- and -tetracarboxylic acids, such as, for example, succinic acid, propanetricarboxylic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid and alkyl- and alkenylsuccinic acids having  $C_2$ - to  $C_{16}$ -alkyl- or -alkenyl radicals;

20 C<sub>4</sub>- to C<sub>20</sub>-hydroxycarboxylic acids, such as, for example, malic acid, tartaric acid, gluconic acid, glutaric acid, citric acid, lactobionic acid and sucrose mono-, di- and tricarboxylic acid;

aminopolycarboxylic acids, such as, for example, nitrilotriacetic acid, ß-alaninediacetic acid, ethylenediaminetetraacetic acid, serinediacetic acid, isoserinediacetic acid, alkylethylenediaminetriacetates, N,N-bis(carboxymethyl)glutamic acid, ethylenediaminedisuccinic acid and N-(2-hydroxyethyl)iminodiacetic acid, methyland ethylglycinediacetic acid.

Examples of oligomeric or polymeric carboxylic acids which are suitable as organic cobuilders are: oligomaleic acids, as are described, for example, in EP-A 451508 and EP-A 396303;

co- and terpolymers of unsaturated C<sub>4</sub>- to C<sub>8</sub>-dicarboxylic acids, the copolymerized comonomers being monoethylenically unsaturated monomers from group (i), given below, in amounts of up to 95% by weight, from group (ii) in amounts of up to 60% by weight and from group (iii) in amounts of up to 20% by weight.

Examples of unsaturated C<sub>4</sub>- to C<sub>8</sub>-dicarboxylic acids in this context are maleic acid, fumaric acid, itaconic acid and citraconic acid. Preference is given to maleic acid.

Group (i) includes monoethylenically unsaturated C<sub>3</sub>-C<sub>8</sub>-monocarboxylic acids, such as, for example, acrylic acid, methacrylic acid, crotonic acid and vinylacetic acid. From group (i), preference is given to using acrylic acid and methacrylic acid.

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Group (ii) includes monoethylenically unsaturated  $C_2$ - to  $C_{22}$ -olefins, vinyl alkyl ethers having  $C_1$ - to  $C_8$ -alkyl groups, styrene, vinyl esters of  $C_1$ - to  $C_8$ -carboxylic acids, (meth)acrylamide and vinylpyrrolidone. From group (ii), preference is given to using  $C_2$ - to  $C_6$ -olefins, vinyl alkyl ethers having  $C_1$ - to  $C_4$ -alkyl groups, vinyl acetate and vinyl propionate.

If the polymers of group (ii) contain copolymerized vinyl esters, some or all of the latter can also be present in hydrolyzed form to give vinyl alcohol structural units. Suitable co-and terpolymers are known, for example, from US-A 3887806 and DE-A 4313909.

Group (iii) includes (meth)acrylic esters of  $C_{l}$ - to  $C_{8}$ -alcohols, (meth)acrylonitrile, (meth)acrylamides of  $C_{l}$ - to  $C_{8}$ -amines, N-vinylformamide and N-vinylimidazole.

Also suitable as organic cobuilders are homopolymers of monoethylenically unsaturated  $C_3$ - $C_8$ -monocarboxylic acids, such as, for example, acrylic acid, methacrylic acid, crotonic acid and vinylacetic acid, in particular acrylic acid and methacrylic acid;

copolymers of dicarboxylic acids, such as, for example, copolymers of maleic acid and acrylic acid in the weight ratio 10:90 to 95:5, particularly preferably those in the weight ratio 30:70 to 90:10 with molar masses of from 1000 to 150 000; terpolymers of maleic acid, acrylic acid and a vinyl ester of a C<sub>1</sub>-C<sub>3</sub>-carboxylic acid in the weight ratio 10 (maleic acid) :90 (acrylic acid + vinyl ester) to 95 (maleic acid) :10 (acrylic acid + vinyl ester), where the weight ratio of acrylic acid to the vinyl ester can vary within the range from 30:70 to 70:30;

copolymers of maleic acid with  $C_2$ - $C_8$ -olefins in the molar ratio 40:60 to 80:20, copolymers of maleic acid with ethylene, propylene or isobutene in the molar ratio 50:50 being particularly preferred.

Graft polymers of unsaturated carboxylic acids onto low molecular weight carbohydrates or hydrogenated carbohydrates, cf. US-A 5227446, DE-A 4415623 and DE-A 4313909, are likewise suitable as organic cobuilders.

- Examples of suitable unsaturated carboxylic acids in this context are maleic acid, fumaric acid, itaconic acid, citraconic acid, acrylic acid, methacrylic acid, crotonic acid and vinylacetic acid, and also mixtures of acrylic acid and maleic acid which are grafted on in amounts of from 40 to 95% by weight, based on the component to be grafted.
- For modification, it is additionally possible for up to 30% by weight, based on the component to be grafted, of further monoethylenically unsaturated monomers to be present in copolymerized form. Suitable modifying monomers are the abovementioned monomers of groups (ii) and (iii).
- Suitable graft bases are degraded polysaccharides, such as, for example, acidically or enzymatically degraded starches, inulins or cellulose, protein hydrolyzates and reduced (hydrogenated or reductively aminated) degraded polysaccharides, such as, for example, mannitol, sorbitol, aminosorbitol and N-alkylglucamine, and also polyalkylene glycols with molar masses up to M<sub>w</sub> = 5000, such as, for example, polyethylene glycols, ethylene oxide/propylene oxide/propylene oxide or ethylene oxide/butylene oxide/propylene oxide/butylene oxide block copolymers and alkoxylated mono- or polyhydric C<sub>1</sub>- to C<sub>22</sub>-alcohols (cf. US-A-5756456).
- Polyglyoxylic acids suitable as organic cobuilders are described, for example, in EP-B-001004, US-A-5399286, DE-A-4106355 and EP-A-656914. The end groups of the polyglyoxylic acids may have different structures.

Polyamidocarboxylic acids and modified polyamidocarboxylic acids suitable as organic cobuilders are known, for example, from EP-A-454126, EP-B-511037, WO-A-94/01486 and EP-A-581452.

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In particular, polyaspartic acids or cocondensates of aspartic acid with further amino acids,  $C_4$ - to  $C_{25}$ -mono- or -dicarboxylic acids and/or  $C_4$ - to  $C_{25}$ -mono- or -diamines are also used as organic cobuilders. Particular preference is given to using polyaspartic acids which have been prepared in phosphorus-containing acids and modified with  $C_6$ - to  $C_{22}$ -mono- or -dicarboxylic acids or with  $C_6$ - to  $C_{22}$ -mono- or -diamines.

Also suitable as organic cobuilders are iminodisuccinic acid, oxydisuccinic acid, aminopolycarboxylates, alkylpolyaminocarboxylates, aminopolyalkylenephosphonates, polyglutamates, hydrophobically modified citric acid, such as, for example, agaric acid, poly-α-hydroxyacrylic acid, N-acylethylenediaminetriacetates, such as lauroyl ethylenediaminetriacetate and alkylamides of ethylenediaminetetraacetic acid, such as EDTA-tallow amide.

Furthermore, it is also possible to use oxidized starches as organic cobuilders.

Further suitable (co)builders are described in WO 99/19435.

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In a further preferred embodiment, the detergents comprising the cosurfactants to be used in accordance with the invention additionally comprise, in particular in addition to the inorganic builders, the anionic surfactants and/or the nonionic surfactants, 0.5 to 20% by weight, in particular 1 to 10% by weight, of glycine-N,N-diacetic acid derivatives, as described in WO 97/19159.

It is also frequently expedient to add bleaching systems, consisting of bleaches, such as, for example, perborate, percarbonate, and optionally bleach activators, such as, for example, tetraacetylethylenediamine, + bleach stabilizers and optionally bleach catalysts to the detergents comprising the cosurfactants to be used in accordance with the invention.

In these cases, the detergents comprising the cosurfactants to be used in accordance with the invention additionally comprise 0.5 to 30% by weight, in particular 5 to 27% by weight, especially 10 to 23% by weight, of bleaches in the form of percarboxylic acids, e.g. diperoxododecanedicarboxylic acid, phthalimidopercaproic acid, or monoperoxophthalic acid or -terephthalic acid, adducts of hydrogen peroxide with inorganic salts, e.g. sodium perborate monohydrate, sodium perborate tetrahydrate, sodium carbonate perhydrate or sodium phosphate perhydrate, adducts of hydrogen peroxide with organic compounds, e.g. urea perhydrate, or of inorganic peroxo salts, e.g. alkali metal persulfates or peroxodisulfates, optionally in combination with 0 to 15% by weight, preferably 0.1 to 15% by weight, in particular 0.5 to 8% by weight, of bleach activators.

#### Suitable bleach activators are:

- polyacylated sugars, e.g. pentaacetylglucose;

- acyloxybenzenesulfonic acids and alkali metal and alkaline earth metal salts thereof, e.g. sodium p-nonanoyloxybenzenesulfonate or sodium p-benzoyloxybenzenesulfonate;
- N,N-diacylated and N,N,N',N'-tetraacylated amines, e.g. N,N,N',N'-tetraacetyl5 methylenediamine and -ethylenediamine (TAED), N,N-diacetylaniline, N,Ndiacetyl-p-toluidine or 1,3-diacylated hydantoins, such as 1,3-diacetyl-5,5dimethylhydantoin;
  - N-alkyl-N-sulfonylcarbonamides, e.g. N-methyl-N-mesylacetamide or N-methyl-N-mesylbenzamide;
- 10 N-acylated cyclic hydrazides, acylated triazoles or urazoles, e.g. monoacetylmaleic hydrazide;
  - O,N,N-trisubstituted hydroxylamines, e.g. O-benzoyl-N,N-succinylhydroxylamine, O-acetyl-N,N-succinylhydroxylamine or O,N,N-triacetylhydroxylamine;
- N,N'-diacylsulfurylamides, e.g. N,N'-dimethyl-N,N'-diacetylsulfurylamide or N,N'-diethyl-N,N'-dipropionylsulfurylamide;
  - acylated lactams, such as, for example, acetylcaprolactam, octanoylcaprolactam, benzoylcaprolactam or carbonylbiscaprolactam;
  - anthranil derivatives, such as, for example, 2-methylanthranil or 2-phenylanthranil;
  - triacyl cyanurates, e.g. triacetyl cyanurate or tribenzoyl cyanurate;
- oxime esters and bisoxime esters, such as, for example, O-acetylacetone oxime or bisisopropyliminocarbonate;
  - carboxylic anhydrides, e.g. acetic anhydride, benzoic anhydride, m-chlorobenzoic anhydride or phthalic anhydride;
  - enol esters, such as, for example, isopropenyl acetate;
- 25 1,3-diacyl-4,5-diacyloxyimidazolines, e.g. 1,3-diacetyl-4,5-diacetoxyimidazoline;
  - tetraacetylglycoluril and tetrapropionylglycoluril;
  - diacylated 2,5-diketopiperazines, e.g. 1,4-diacetyl-2,5-diketopiperazine;
  - ammonium-substituted nitriles, such as, for example, N-methylmorpholinium acetonitrile methylsulfate;
- of propylenediurea and 2,2-dimethylpropylenediurea, e.g. tetraacetylpropylenediurea;
  - α-acyloxypolyacylmalonamides, e.g. α-acetoxy-N,N'-diacetylmalonamide;
  - diacyldioxohexahydro-1,3,5-triazines, e.g. 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine;
- benz-(4H)1,3-oxazin-4-ones having alkyl radicals, e.g. methyl, or aromatic radicals, e.g. phenyl, in the 2-position;
  - cationic nitriles, as described in DE-A-101 48 577.

The described bleaching system comprising bleaches and bleach activators can optionally also comprise bleach catalysts. Examples of suitable bleach catalysts are quaternized imines and sulfonimines, which are described, for example, in US-A 5 360 569 and EP-A 453 003. Particularly effective bleach catalysts are manganese complexes, which are described, for example, in WO-A 94/21777. Where used, such compounds are incorporated into the detergents in amounts of at most up to 1.5% by weight, in particular up to 0.5% by weight, and in the case of very active manganese complexes, in amounts up to 0.1% by weight. Further suitable bleach catalysts are described in WO 99/19435.

Further bleaching systems based on arylimidoperalkanoic acids which can be used are described in EP-A-0 325 288 and EP-A-0 490 409.

#### Bleach stabilizer

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These are additives which are able to absorb, bind or complex traces of heavy metals. Examples of additives with a bleach-stabilizing action which can be used according to the invention are polyanionic compounds, such as polyphosphates, polycarboxylates, polyhydroxypolycarboxylates, soluble silicates as completely or partially neutralized alkali metal or alkaline earth metal salts, in particular as neutral Na or Mg salts which are relatively weak bleach stabilizers. Strong bleach stabilizers which can be used according to the invention are, for example, complexing agents, such as ethylenediamine tetraacetate (EDTA), nitrilotriacetic acid (NTA), methylglycinediacetic acid (MGDA), β-alaninediacetic acid (ADA), ethylenediamine N,N'-disuccinate (EDDS) phosphonates, such as ethylenediaminetetramethylenephosphonate, diethylenetriaminepentamethylenephosphonate or hydroxyethylidene-1,1-diphosphonic acid in the form of the acids or as partially or completely neutralized alkali metal salts. The complexing agents are preferably used in the form of their Na salts.

As well as the described bleaching system comprising bleaches, bleach activators and optionally bleach catalysts, the use of systems with enzymatic peroxide release or of photoactivated bleaching systems is also possible for the detergents comprising the cosurfactants to be used in accordance with the invention, see e.g. US 4,033,718.

For a number of uses, it is expedient for the detergents comprising the cosurfactants to be used in accordance with the invention to comprise enzymes. Enzymes which are preferably used in detergents are proteases, amylases, lipases and cellulases. Preferred amounts of the enzymes are from 0.1 to 1.5% by weight, particularly preferably 0.2 to 1.0% by weight, of the formulated enzyme. Examples of suitable proteases are Savinase and Esperase. A suitable lipase is e.g. Lipolase. A suitable cellulase is e.g. Celluzym. The use of

peroxidases for activating the bleaching system is also possible. It is possible to use individual enzymes or a combination of different enzymes. Where appropriate, the detergent comprising the cosurfactants to be used in accordance with the invention can also comprise enzyme stabilizers, e.g. calcium propionate, sodium formate or boric acids or salts thereof, and/or antioxidants.

The constituents of detergents are known in principle to the person skilled in the art. The lists, above and below, of suitable constituents give merely an illustrative selection of the known suitable constituents.

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In addition to the main components stated hitherto, the detergents comprising the cosurfactants to be used in accordance with the invention can also comprise the following further customary additives in the amounts customary for this purpose:

Known dispersants, such as naphthalenesulfonic acid condensates or polycarboxylates, soil-carrying agents, soil release agents, such as polyether esters, incrustation inhibitors, pH-regulating compounds, such as alkalis or alkali donors (NaOH, KOH, pentasodium metasilicate, sodium carbonate) or acids (hydrochloric acid, phosphoric acid, amidosulfuric acid, citric acid), buffer systems, such as acetate or phosphate buffer, ion exchangers, perfume, dyes, graying inhibitors, optical (fluorescent) brighteners, color-transfer inhibitors, such as, for example, polyvinylpyrrolidone, biocides, such as isothiazolinones or 2-bromo-2-nitro-1,3-propanediol, hydrotropic compounds as solubility promoters or solubilizers, such as cumenesulfonates, toluenesulfonates, short-chain fatty acids, urea, alcohols or phosphoric alkyl/aryl esters, foam regulators for stabilizing or suppressing foam, e.g. silicone oils, skin and corrosion protectants, disinfecting compounds or systems, such as, for example, those which release chlorine or hypochlorous acid, such as dichloroisocyanurate or which contain iodine, thickeners and extenders and formulating agents.

## 30 Graying inhibitors and soil release polymers

Suitable soil release polymers and/or graying inhibitors for detergents are for example:

polyesters of polyethylene oxides with ethylene glycol and/or propylene glycol and aromatic dicarboxylic acids or aromatic and aliphatic dicarboxylic acids;

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polyesters of unilaterally terminally capped polyethylene oxides with di- and/or polyhydric alcohols and dicarboxylic acid.

Such polyesters are known, for example from US-A 3,557,039, GB-A 1 154 730, EP-A-185 427, EP-A-241 984, EP-A-241 985, EP-A-272 033 and US-A 5,142,020.

Further suitable soil release polymers are amphiphilic graft or copolymers of vinyl and/or acrylic esters onto polyalkylene oxides (cf. US-A 4,746,456, US-A 4,846,995, DE-A-37 11 299, US-A 4,904,408, US-A 4,846,994 and US-A 4,849,126) or modified celluloses, such as, for example, methylcellulose, hydroxypropylcellulose or carboxymethylcellulose.

#### 10 Color transfer inhibitors

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The color transfer inhibitors used are, for example, homo- and copolymers of vinylpyrrolidone, of vinylimidazole, of vinyloxazolidone and of 4-vinylpyridine N-oxide having molar masses of from 15 000 to 100 000, and crosslinked finely divided polymers based on these monomers. The use mentioned here of such polymers is known, cf. DE-B-22 32 353, DE-A-28 14 287, DE-A-28 14 329 and DE-A-43 16 023.

Suitable polyvinylpyridinebetaines are described, for example in Tai, Formulating Detergents and Personal Care Products, AOCS Press, 2000, page 113.

In addition to the use in detergents and cleaners for domestic textile washing, the detergent compositions which can be used according to the invention can also be used in the field of commercial textile washing and of commercial cleaning. In this field of use, peracetic acid is usually used as bleach, and is added to the wash liquor as an aqueous solution.

#### 25 Use in textile detergents

A typical pulverulent or granular heavy-duty detergent according to the invention may, for example, have the following composition:

- 0.5 to 50% by weight, preferably 5 to 30% by weight, of at least one anionic and/or nonionic surfactant, including the cosurfactants according to the invention,
  - 0.5 to 60% by weight, preferably 15 to 40% by weight, of at least one inorganic builder,
  - 0 to 20% by weight, preferably 0.5 to 8% by weight, of at least one organic cobuilder,
  - 2 to 35% by weight, preferably 5 to 30% by weight, of an inorganic bleach,
- 0.1 to 20% by weight, preferably 0.5 to 10% by weight, of a bleach activator, optionally in a mixture with further bleach activators,
  - 0 to 1% by weight, preferably up to at most 0.5% by weight, of a bleach catalyst,
  - 0 to 5% by weight, preferably 0 to 2.5%, of a polymeric color transfer inhibitor,

- 0 to 1.5% by weight, preferably 0.1 to 1.0% by weight, of protease,
- 0 to 1.5% by weight, preferably 0.1 to 1.0% by weight, of lipase,
- 0 to 1.5% by weight, preferably 0.2 to 1.0% by weight, of a soil release polymer,
- 5 ad 100% of customary auxiliaries and adjuncts and water.

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Inorganic builders preferably used in detergents are sodium carbonate, sodium hydrogencarbonate, zeolite A and P, and amorphous and crystalline Na silicates, and also phyllosilicates.

Organic cobuilders preferably used in detergents are acrylic acid/maleic acid copolymers, acrylic acid/maleic acid/vinyl ester terpolymers and citric acid.

Inorganic bleaches preferably used in detergents are sodium perborate and sodium carbonate perhydrate.

Anionic surfactants preferably used in detergents are linear and slightly branched alkylbenzenesulfonates (LAS), fatty alcohol sulfates/ether sulfates and soaps.

Enzymes preferably used in detergents are protease, lipase, amylase and cellulase. For the commercially available enzymes, amounts of from 0.05 to 2.0% by weight, preferably 0.2 to 1.5% by weight, of the formulated enzyme, are generally added to the detergent. Suitable proteases are, for example, Savinase, Desazym and Esperase. A suitable lipase is, for example, Lipolase. A suitable cellulase is, for example, Celluzym.

Soil release polymers and graying inhibitors preferably used in detergents are graft polymers of vinyl acetate onto polyethylene oxide of molar mass 2500-8000 in the weight ratio 1.2:1 to 3.0:1, polyethylene terephthalates/oxyethylene terephthalates of molar mass 3000 to 25 000 from polyethylene oxides of molar mass 750 to 5000 with terephthalic acid and ethylene oxide and a molar ratio of polyethylene terephthalate to polyoxyethylene terephthalate of from 8:1 to 1:1, and block polycondensates according to DE-A-44 03 866.

Color transfer inhibitors preferably used in detergents are soluble NVP homopolymers and/or vinylpyrrolidone and vinylimidazole copolymers with molar masses greater than 5000.

The detergents are often in solid, pulverulent form, in which case they usually additionally comprise customary extenders, which give them good flowability, dosability and solubility and which prevent caking and dusting, such as sodium sulfate or magnesium sulfate.

The pulverulent or granular detergents according to the invention can comprise up to 60% by weight of inorganic extenders. However, the detergents according to the invention preferably have a low content of extenders and comprise only up to 20% by weight, particularly preferably only up to 8% by weight, of extenders.

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Detergents comprising the cosurfactants to be used in accordance with the invention can have various bulk densities in the range from 300 to 1200, in particular 500 to 950 g/l. Modern compact detergents usually have high bulk densities and are granular in structure. Compact or ultracompact detergents and extrudates have a bulk density of > 600 g/l. These are becoming more important.

If they are to be used in liquid form, they may be in the form of aqueous microemulsions, emulsions or solutions. In liquid detergents, solvents such as ethanol, isopropanol, 1,2-propylene glycol or butyl glycol can additionally be used.

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In the case of gel detergents thickeners, such as, for example, polysaccharides and/or weakly crosslinked polycarboxylates (for example Carbopol® from Goodrich) can additionally be used.

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In the case of tablet detergents, tableting auxiliaries, such as, for example, polyethylene glycols with molar masses of > 1000 g/mol, polymer dispersions, and tablet disintegrants such as cellulose derivatives, crosslinked polyvinylpyrrolidone, crosslinked polyacrylates or combinations of acids, e.g. citric acid + sodium bicarbonate, to name but a few, are additionally required.

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The present invention further provides for the use of the mixtures in the preparation of detergents.

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In connection with the present invention, the term "cleaners" is generally understood as meaning formulations which are used for cleaning hard surfaces. They are in liquid, gel, paste or solid form. Materials which are a type of solid form include powders and compacts, such as, for example granulates and shaped bodies, for example tablets. Examples include hand dishwashing detergents, machine dishwashing detergents, metal degreasers, glass cleaners, floor cleaners, all-purpose cleaners, high-pressure cleaners, alkaline cleaners, acidic cleaners, spray degreasers, dairy cleaners, upholstery cleaners, plastics cleaners and bath cleaners. They comprise 0.01 to 40% by weight, preferably 0.1

to 25% by weight, based on the total formulation, of at least one substance of the formulae I and/or II. Further constituents are detailed below.

- ionic surfactants, such as, for example, alcohol sulfate/ether sulfates, alkylbenzene sulfonates, α-olefinsulfonates, sulfosuccinates, as described above under "detergents".
  - nonionic surfactants, such as, for example, alcohol alkoxylates, alkylamine alkoxylates, alkylamide ethoxylates, alkyl polyglucosides, as described above under "detergents".
- amphoteric surfactants, such as, for example, alkylamine oxides, betaines, as described above under "detergents".
  - builders, such as, for example, polyphosphates, polycarboxylates, phosphonates, complexing agents, e.g. methylglycine diacetic acid and salts thereof, nitrilotriacetic acid and salts thereof, ethylenediamine tetraacetic acid and salts thereof, as described above under "detergents".
  - dispersants, such as, for example, naphthalenesulfonic acid condensates, polycarboxylates, as described above under "detergents".
  - pH-regulating compounds, such as, for example, alkalis (NaOH, KOH, pentasodium metasilicate) or acids (hydrochloric acid, phosphoric acid, amidosulfuric acid, citric acid)
  - enzymes, such as, for example lipases, amylases, proteases
  - perfume
  - dyes

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- biocides, such as, for example, isothiazolinones, 2-bromo-2-nitro-1,3-propanediol, as described above under "detergents".
  - bleaching systems, consisting of bleaches, such as, for example, perborate, percarbonate etc., plus bleach activators, such as, for example, tetraacetylethylenediamine, plus bleach stabilizers, as described above under "detergents".
- Solubilizers, such as, for example cumenesulfonates, toluenesulfonates, short-chain fatty acids, phosphoric alkyl/aryl esters
  - solvents, such as, for example, short-chain alkyl oligoglycols, such as butyl glycol, butyl diglycol propylene glycol monomethyl ether, alcohols, such as ethanol, isopropanol, aromatic solvents, such as toluene, xylene, N-alkylpyrrolidones, alkylene carbonates.

The constituents of cleaners for hard surfaces are known in principle to the person skilled in the art. The above list represents merely an exemplary section of the constituents.

The cleaners for hard surfaces are usually, but not exclusively, aqueous and are in the form of microemulsions, emulsions or solutions.

Where they are present in solid, pulverulent form, extenders, such as, for example, sodium sulfate, magnesium sulfate, etc. may additionally be used.

In the case of cleaners in the form of tablets, tableting auxiliaries, such as, for example, polyethylene glycols with molar masses > 1000 g/mol, polymer dispersions etc., and tablet disintegrants, such as, for example, cellulose derivatives, crosslinked polyvinylpyrrolidone, crosslinked polyacrylates or combinations of acids, e.g. citric acid plus sodium bicarbonate, to name but a few, are additionally required.

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Products from the bodycare sector are, for example, shampoos, shower and bath gels, shower and bath lotions, lipsticks and cosmetic formulations with care and/or conditioning properties, such as styling products. Examples are hair foams, hair gels, hair sprays or after-treatment compositions, such as hair tonics, lotions, treatment rinses, treatment packs, split-end fluids, hair repair compositions, "hot oil treatments", shampoos, liquid soaps, care creams, hair-setting compositions, hair colorants and permanent waving compositions. When used in bodycare products, the substances according to the formulae I and II have the advantage that the physiological irritantancy of the surfactant mixtures is moderated and the mucous membranes are protected.

25 The invention is now illustrated in the examples below.

## Example 1

#### 3,5-Bis(1-ethylpentyl)-7a-hydroxymethyldihydrooxazolo[3,4-c]oxazole

0.55 mol of ethylhexanal, 0.25 mol of tris(hydroxymethyl)aminomethane and 0.25 g of Amberlyst 15 are mixed at room temperature. The reaction mixture is heated to 100°C at 500 mbar. The water which forms distills off over the course of 3 hours. The mixture is then left to cool to room temperature and filtered. The reaction product can be used without further purification.

## Example 2

# $3,5-B is (1-ethylpentyl)-7 a-hydroxymethyldihydrooxazolo \\ [3,4-c] oxazole$

The reaction was carried out in a distillation apparatus. 256 g (2.0 mol) of 2-ethylhexanal were combined with 121 g (1.0 mol) of tris-hydroxymethylaminomethane at room temperature. The mixture was then heated to 100°C at a pressure of 500 mbar. After 1 l at 500 mbar/100°C, the pressure is reduced to 250 mbar until distillate no longer passed over. The distillate collected was 2-phase. The phase containing ethylhexanal was returned to the reaction mixture and stirred again for 1 h at 500 bar and 100°C. The product can be used without further purification.

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#### Example 3

## 2-(1-Ethylpentyl)4,4-di(hydroxymethyl)oxazolidine

1.5 mol of 2-ethylhexanal, 1.5 mol of tris(hydroxymethyl)aminomethane and 1.5 g of Amberlyst 15 were mixed at room temperature with 300 ml of toluene. The mixture is boiled for three hours with a water separator until no new water is collected. The mixture is then allowed to cool to room temperature and filtered, and the solvent is evaporated under reduced pressure. The product can be used without further purification.

## Example 4

# 7a-Hydroxymethyl-3,5-di(dodecyl)dihydrooxazolo[3,4-c]oxazole/7a-hydroxymethyl-3,5-di(tetradecyl)dihydrooxazolo[3,4-c]oxazole

0.85 mol of C13/C15-aldehyde mixture, 0.39 mol of tris(hydroxymethyl)aminomethane and 0.4 g of Amberlyst 15 are mixed at room temperature. The reaction mixture is heated to 100°C at 500 mbar. The water which forms is distilled over the course of 3 hours. The mixture is then left to cool to room temperature and filtered. The reaction product can be used without further purification.

#### Example 5

# ${\bf 4,4-Di(hydroxymethyl)-2-dodecyloxazolidine/4,4-di(hydroxymethyl)-2-tetradecyloxazolidine}$

1.5 mol of C13/C15-aldehyde mixture, 1.5 mol of tris(hydroxymethyl)aminomethane and 1.5 g of Amberlyst® 15 were mixed with 300 ml of toluene at room temperature. The mixture is boiled for three hours using a water separator until no more new water is collected. The mixture is then left to cool to room temperature and filtered, and the solvent is evaporated under reduced pressure. The product can be used without further purification.

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## Example 6

## 2-(1-Ethylpentyl)-[1,3]-dioxolan-4-one

0.50 mol (64.1 g) of 2-ethylhexanal and 0.3 g of Amberlyst® 15 were added to 150 ml of chloroform at room temperature. The water separator was filled with 50 ml of chloroform and the reaction mixture was refluxed (93°C). 0.50 mol (50.0 g) of lactic acid (90% aqueous solution) was slowly added dropwise and stirred under reflux until 19 ml of  $H_2O$  had been separated off. Finally, the Amberlyst® 15 was filtered off and the product was purified by distillation.

#### 10 Example 7

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## Hand dishwashing detergent

A model formulation comprising 30% by weight of Lutensit® ALBN50 (BASF AG, alkylbenzenesulfate, 50%), 10% by weight of Lutensol® AO7 (BASF AG, C13/15, alcohol ethoxylate, 7 ethylene oxide, 100%), 3% by weight of 3,5-bis-(1-ethylpentyl)-7a-hydroxymethyldihydrooxazolo[3,4-c]oxazole is admixed with various amounts of Lutensol® A3N (BASF AG, C12,14-alcohol ethoxylate, 3EO, 100% BASF AG). The resulting mixtures are analyzed using an Uhbelohde viscometer, spindle 3, shear rate 3 s<sup>-1</sup>. In parallel experiments, a corresponding surfactant mixture in which the reaction product was replaced by Mazox® LDA (laurylamine oxide, 100%, origin BASF Corporation) and by water were investigated. The results are summarized in the table. The viscosity increase is most marked for the product according to the invention.

0	1	2	4	6	8	% Lutensol® A3N
892	2900	6760	30000	172000		3,5-bis-(1-ethylpentyl)-7a-hydroxy-
						methyldihydrooxazolo[3,4-c]oxazole
1210	905	970	1820	2890	7010	Water
2040	2500	2910	5760	12700	19200	Mazox LDA Oxide w.s.

#### Example 8

#### Hand dishwashing detergent

Foam stabilization with 3,5-bis(1-ethylpentyl)-7a-hydroxymethyldihydrooxazolo[3,4-c]oxazole.

A model formulation comprising 30% by weight of Lutensit® ALBN50 (alkylbenzenesulfate, 50%), 10% by weight of Lutensol® AO7 (C13/15, alcohol ethoxylate, 7 ethylene oxide, 100%), 3% by weight of 3,5-bis(1-ethylpentyl)-7a-hydroxymethyldihydrooxazolo[3,4-c]oxazole and 3% by weight of Lutensol A3N (C12,14-alcohol ethoxylate, 3EO, 100%) is diluted to 2% by weight of surfactant. In a beaker (5 l in

volume, filled to 21), this surfactant solution is added to the foam by stirring. When a stable state has been established, fresh olive oil is added dropwise until the foam has disappeared. The amount of oil necessary for this is a measure of the stability of the foam. In parallel experiments, a corresponding surfactant mixture in which the reaction product was replaced by Mazox® LDA (laurylamine oxide, 100%) and by water were investigated. The results are summarized in the table.

Additive	Consumption of olive
	oil
3,5-Bis(1-ethylpentyl)-7a-hydroxymethyldihydrooxazolo[3,4-	37 ml
c]oxazole + 3 EO	
Mazox® LDA	28 ml
Water	27 ml